

Tutorial 4.2 — Liquid Scintillation Counting

Slide 1. Liquid Scintillation Counting

The topic of this module is the theory and analysis of samples using liquid scintillation. This is the first module where we will see the relationship between radioactive decay events and nuclear instrumentation detection.

Slide 2. Learning Objectives

When you have completed this lesson you will be able to

- Identify the components of a liquid scintillation cocktail and describe their function as it relates to energy transfer.
- Define the terms as they relate to liquid scintillation counting:
 - Background,
 - Coincidence circuit,
 - Quench,
 - QIP,
 - Efficiency, and
 - Quench curve.
- Describe how the “H Number” is determined and how it relates to counting efficiency.
- Examine a liquid scintillation spectrum to identify possible contamination from other radionuclides.

The key concepts to be covered in this lesson are:

- Liquid scintillation Counting may be the only viable detection option for some types of radionuclides.
- Instrument background activity must be measured for each batch of samples and used to correct sample activity.
- Quench correction must be performed when calculating the amount of activity in each sample.
- Different instruments use different Quench Indicating Parameters (QIPs). These QIPs use different means of displaying the quench curves.

Slide 3. What is Liquid Scintillation Counting?

Liquid scintillation counting is a method that takes advantage of the way particles transfer energy to matter *without* causing ionization. In our beginning modules we discussed that one of the ways that alpha and beta particles can lose energy with their surrounding matter is by causing excitation. In liquid scintillation we rely exclusively on this property to allow us to measure how much of a radionuclide is present. Liquid scintillation is used primarily for analysis of radionuclides that decay by beta particle emission. It can be used for analysis of radionuclides that decay by alpha and low energy gamma as well. However this presentation focuses on the beta particle analysis part of this method.

There are two parts to this process that make it imperative that chemical separations be very effective at isolating the radionuclide of interest:

1. Beta particles do not have a unique energy of decay.
2. The form of energy transfer, excitation, does not have a single value for the energy transferred.

Thus if we don't have effective chemical separation it will not be easy to distinguish one beta emitter from another.

Liquid scintillation is the most practical method of analysis and the one that is most easily accommodated by production laboratories for radionuclides that are —

- “Beta only” emitters,
- Low to mid range beta energy (0.05 to 0.20 MeV), or
- Volatile radionuclides (like tritium).

These characteristics make liquid scintillation ideal for analysis of tritium. We will discuss tritium analysis in detail in the next module.

Slide 4. How Liquid Scintillation Works

The process of liquid scintillation relies on the transfer of kinetic energy from the beta particle to the solution components through a series of energy transformations. The first involves the initial transfer of kinetic energy to the solvent molecules bringing them to an excited state. This excited state is sometimes referred to as an excimer. The greater the energy of the beta particle the greater will be the number of solvent molecules that become excimers. The excimer then releases this energy very quickly in the form of ultraviolet radiation. The released ultraviolet light then excites fluor molecules in the solvent. The fluor molecules will then release the energy in the UV-Visible range of energy of 300-450 nanometers.

You might ask, “Why not just use fluor molecules in place of the solvent”? The solvent maintains the fluor in solution with the aqueous sample to be analyzed and does not allow the phases to separate. The key factor in liquid scintillation is that the beta emitters in the aqueous phase be homogeneously mixed with the fluor for efficient energy transfer.

Slide 5. How Liquid Scintillation Works — Slide 2

The two components, the aqueous sample and the scintillation solution (called a *cocktail*) are mixed in a vial that has a volume of about 20 mL. The specific ratio of sample to scintillator solution is dependent upon the radionuclide, the instrument and the fluor material. The vial that contains the mixture is then sandwiched between two photomultiplier tubes. This arrangement allows for almost 100% of all emitted radiation from the solution to be impinged on the PM tube surface.

The fluor molecule emits its excited state radiation equally in all directions. Since more than one molecule is excited for each beta particle decay event, if both PM tubes detect a flash of light from the scintillation vial within a certain time frame, it is relatively certain that the light flash was due to a beta decay event. This synchronization of the two PM tubes is referred to as *coincidence counting*. We will discuss this phenomenon in more detail later on in this module.

One other aspect of the detection system is that it records each event in a location called a channel. The channel is a file that contains the number of events recorded during the counting interval at a particular energy. When the sample has finished counting, a plot of the number of events versus channel number provides information regarding the number of events of a specific energy versus the energy range of the decay events that occurred in the solution. Since the beta decay energy is not monoergic, these decay events that are registered likewise are not monoergic.

Slide 6. Typical Components of a Liquid Scintillation Cocktail

The table shown on this slide identifies the four constituents of a cocktail. The solvent allows the other three components and the aqueous sample to remain mixed so that the energy transfer process can occur efficiently. The fluor is the principal component as it emits the UV-Visible light in the range acceptable for effective conversion into an electronic pulse by the PM tube. The secondary fluor sometimes referred to as a “wave-shifter” allows more effective production of UV-Visible light from high energy beta particles after they have interacted with the primary fluor. Finally the surfactant molecule enhances the miscibility of the aqueous sample and the cocktail materials.

Slide 7. The Cocktail is the Detector

Based on our discussion in the previous slides it becomes obvious that the actual detector in the liquid scintillation process is the cocktail. Low to mid energy beta particles are completely stopped within the solution, transferring all of their energy to the cocktail via the various energy transfer processes. Anything that changes in this relationship, the ratio of solvent to cocktail, the type of contaminant in the solution, the type of cocktail, etc will affect the energy transfer process.

Slide 8. Detection of Low to Mid-energy Beta Emitters

The table shown on this slide identifies beta emitting radionuclides that are routinely determined using liquid scintillation analysis. In order for a beta particle to be effective in exciting fluor molecules it needs to have a minimum energy of about 4 keV. The table also shows the maximum beta particle energy for each radionuclide. Every beta particle emitter has a continuum of energies from the maximum energy down to almost zero for each radionuclide. Keep in mind that the greatest numbers of emitted beta particles have energies that are approximately one third of the beta maximum value. Thus for tritium the average energy is about 6 keV, which also means that a substantial number of the beta particles for tritium are going to be less than this value. For tritium about 35% of all emitted beta particles have energies less than 4 keV. This means that the maximum efficiency for detection for tritium will be about 65%.

Slide 9. Background Counts

The organic molecules that comprise the cocktail may be excited by other means besides radioactive decay. Heat, normal room light or sunlight, static charge, and chemical reactions can cause these fluor molecules to become excited and yield UV-Visible light that is detected by the PM tubes. This means that if we prepare a pure water blank with no radionuclides present, mix it with cocktail and count it, we will still get a signal that is

indistinguishable from radioactive decay. We rely on the fact that we can control this background signal by various physical means. Some of which are:

- Preventing room or sun light from interacting with the counting process by enclosing the detection system in a light proof enclosure.
- Controlling the temperature of the room where the liquid scintillation counter is located.
- Purifying the radionuclide of interest from all other radionuclides.
- Selecting reagents that have low levels of contaminants in them; either radioactive or stable.

The manner in which we minimize background radiation is by selecting a region of interest, referred to as the ROI. The ROI is the area of the output spectrum where we find the maximum ratio of sample signal to background signal. In other areas of instrumental analysis this is referred to as maximizing the signal to noise ratio, in radiochemistry it is referred to as the figure of merit. The maximum value for the figure of merit is found by using a standard of the radionuclide of interest and changing the width of the ROI until the maximum value is determined.

Slide 10 Correcting for Background

Background radiation should be constant for the intervals of time over which samples are counted. This means that the higher the activity level in the samples, the smaller will be the effect on the radioactivity measurement. However when we are analyzing samples that are very low in activity, even small backgrounds will have a significant effect on our ability to distinguish radioactivity from a sample from background radioactivity. This means that the analyst must do all they can to reduce background effects.

Good laboratory practices such as —

- Preventing contamination of sample test source (cocktail + sample),
- Removing ambient sources of radiation such as standards or bulk sample storage into another area),
- Selecting reagents and vials that are low in radioactive content,
- Prevent static electricity by using cloths to help eliminate this problem on the vials, and
- Controlling laboratory temperature —

Will all help to maintain a low and constant background.

Some effects we have only minimal capabilities to control. The analyst needs to be aware of how these affect the analyses. These include:

- Electronic noise from power or electromagnetic sources.
- Photo- and chemiluminescence.
- Cosmic radiation.

Thermal “noise” in PMTs also referred to as “dark counts.”

Slide 11. Correcting for Background: Coincidence Circuits

We had noted in an earlier discussion that our liquid scintillation cell is sandwiched between two photomultiplier tubes. This sandwich effect has two beneficial purposes. The first was to maximize the efficiency of collection of the light emitted from the scintillation vial. The second was to afford a more selective way to count only radiation due to radioactive decay. This technique was called coincidence counting. Instruments contain coincidence circuitry that examines when pulses are recorded by each of the two PM tubes. If the event occurs within a very short time frame, about 20 nanoseconds, the circuitry sums the result of the two events and indicates that a radioactive decay has occurred. If the two events in the PM tubes are not within this window of time, no event is recorded. Background events that cause a signal to be registered in the PM tubes that do not come from the scintillation solution will affect one PM tube and not the other. These events are background and the coincidence circuitry eliminates these types of events. This electronic processing of the signals improves the figure of merit for the analysis and allows a lower detection limit.

Slide 12. Background: Luminescence

Organic molecules like the fluors used in the cocktail can be stimulated to excited states by many different forms of energy transfer. These can be heat, room light or sunlight, static charge and chemical reactions. The excited states in these molecules can last from nanoseconds up to hours, depending upon the characteristics of the excited state, and how many of the molecules are in the excited state.

Slide 13: Dark Adapting

One of the excitation processes that cause background counts that we have control over is exposure to room light. Room light has many different wavelengths (from fluorescent bulbs, incandescent bulbs, and sunlight) and different intensities depending on the rooms' individual lamp intensities. Since we cannot prepare samples in the dark, once the sample is mixed with the cocktail we allow the sample to dark adapt in the instrument prior to counting it. The dark adapt period will vary with instrument manufacturer and cocktail but generally is from 15 to 45 minutes. Liquid scintillation instruments are designed to run samples as large batches. The samples are loaded into the instrument at the same time and all dark adapted simultaneously prior to counting. Each radionuclide-cocktail combination may have its own dark adapt period so the analyst must ensure that the standards for the instrument are run using the same protocol as the samples.

Slide 14. About Background in Water Analysis

The background radiation that is measured is minimized by the analyst and the conditions under which the instrument is operated. However we must account for the background radiation in our final analytical result. The backgrounds need to be determined by making a sample test source that:

- Has no radionuclide of interest present.
- Matches the lot of cocktail that is same as that used for samples.
- Has the same chemical make up of the samples to be counted.
- Has approximately the same level of "quench."

- Can be determined with adequate precision to meet the analytical uncertainty requirements.

Once the background counts for a batch of samples is determined, that value will be subtracted from the total counts recorded for each sample.

Slide 15. Quench

In the last slide, we mentioned the term quench and that the instrument background sample quench needed to approximate that of the sample quench. So what is quench? Quench is any process that interferes with the energy transfer of the radioactive decay particle to the fluor and the subsequent detection of the fluor de-excitation energy by the PMT. Ultimately this means fewer counts are recorded.

There are primarily three types of quench. Chemical quenching occurs when a substance in the solution preferentially interacts with the radioactive decay particles and does not transfer the absorbed energy to the solvent or the fluor. Certain electrophilic materials like halogens can cause chemical quench. Another form of quench is color. If a solution has materials in it that can absorb energy like the fluor, but not re-emit it in the proper energy range then the PM tube will not be as effective at detection. The third form of quench is from solution opacity or turbidity. Physical obstructions in the solution that are not transparent to the light emitted by the fluor will diminish the signal received by the PM tube.

Slide 16. Effect of Quenching

The effect of quench is that it reduces the number of decay events that wind up being recorded at the PM tube. Quench also effects the distribution of the particle energies that are measured by the PM tube. The diagram shown on this slide illustrates how the quenched spectrum is not only reduced in magnitude but the position of the maximum counts recorded is also shifted to a lower energy. A quantitative means of determining how much quench has occurred and how quench affects the efficiency of measurement must be applied to the final analysis values for the measurement.

Slide 17. Measuring Quench: Quench Indicating Parameters

As you might expect several different techniques have been developed to measure the degree of quench experienced by an individual solution. The general term for the measurement used to determine quench is called a Quench Indicating Parameter or QIP. Liquid scintillation instruments use sophisticated software to determine the shape or energy characteristics exhibited by each sample solution and compare these to an unquenched standard. The three most common techniques for quench correction used are the H-Number, the Spectral Index of the Sample and the Transformed spectral Index of the External Standard.

Regardless of how quench is measured it is necessary to correct each sample for quench.

Slide 18. Types of QIPs

The slide describes briefly each of the three techniques for measuring QIPs. The technique that is most commonly used is the H-Number method which will be described in the next few slides.

In order to understand how this effect is measured we first need to describe one of the interactions of gamma radiation with matter. Gamma rays of moderate energy can interact with matter by transfer of some of their energy to bound electrons. This is known as the Compton Effect. When this occurs in the liquid scintillation solution, the energy transfer process from these scattered electrons is exactly the same as the energy transfer for a beta particle emitted from a radionuclide within the solution. Thus if we are able to measure the energy distribution of these scattered electrons in our sample and in our unquenched standard the QIP value of the sample can be determined.

Slide 19. The H-Number

Liquid scintillation instruments now contain external standard radioactive material. In the case of the H-Number the external standard is ^{137}Cs . The external standard never comes into contact with the liquid scintillation vial, but the gamma rays that it emits are focused on the solution. The 662 keV gamma rays produce a distribution of Compton Electrons in the solution that behaves just like beta particles emitted during radioactive decay. The intensity of the gamma source requires that the sample only be exposed to the source for a short period of time. The measured events from this exposure are stored in a file separate from the counts made when the sample is not exposed to the source. The ^{137}Cs generated distribution is then compared to the distribution of an unquenched standard. As the figure on the slide shows, the instrument software then determines the inflection points of both curves. The difference in channel number between the two inflection points is the H-Number. The larger the H-Number the larger is the sample quench.

Slide 20. Correlating Quench Values to counting Efficiency (Slide 1 of 2)

The pictogram in this slide shows how the QIP is determined on a practical basis. A set of counting vials are set up and the same volume of liquid standard plus the same volume of liquid cocktail is added to each one. Next, varying amounts of quench agent is added to all the vials except for one. Any material that causes quench may be used. Typically instrument manufacturers suggest adding nitromethane, a chemical quench agent. However any material that will interfere with the energy transfer process will work. Another example identified here is Eriochrome Black T a metallochromic indicator. It provides a significant color quench. Each sample is then counted.

Slide 21. Correlating Quench Values to counting Efficiency (Slide 2 of 2)

The instrument will determine the H-number of each of the solutions as well as the final total counts. Knowing the final total count rates we can now determine the net count rates for each sample by subtracting the background count rate. If we take this net count rate and divide by the original activity added to each sample we will get an efficiency value between zero and one. This can be plotted versus the H-number for each solution. Such a plot is shown on the next slide.

Slide 22. A Typical Quench Curve

Three quench curves are shown on the graph in Slide 22. The y-axis is the efficiency with which a sample decay emission is detected and the x-axis is the quench number. Remember from the definition of the H-Number that it represented the difference in value of the inflection point of the beta particle energy distribution between the standard and the sample. Also remember that a larger value of the H-Number, will indicate more quench, and ultimately lower efficiency. This is exactly the relationship shown on this graph. Note also that the higher the maximum energy of the emitted beta particle the less effect quench has on the efficiency. Other QIPs will yield different shapes to the quench curve.

Slide 23. Liquid Scintillation Plot

The plot on slide 23 shows the response of a quality control sample containing tritium. The instrument has determined the H-Number for this sample as 251.3, and determined that the total number of counts in the region of interest is 1125.

Slide 24. Spectrum Plot Indicating Contamination

The analysis of a sample in the same batch as the quality control sample in the previous slide shows a small shift in the position of the inflection point of the curve (lower H-Number) and also the presence of some higher energy components. Also note the span on the y-axis compared to the previous slide. This sample obviously has lower tritium content than the quality control sample.

Slide 25. Pulse Shape Discrimination

This is a special function of the liquid scintillation instrument that may be purchased as an extra feature. This function can distinguish between alpha and beta interactions based on the size of the pulses and how slowly they decay. It may be used as an effective gross screening tool for samples containing high levels of radioactivity. It is also possible that this feature can be used to eliminate overlap of beta particle spectra if chemical separation is not possible or if chemical separation was ineffective.

Slide 26. Conclusion

Based on the information we have covered in this module you should be able to

- Describe the composition of a cocktail and the function of each constituent.
- Explain how the liquid scintillation instrument functions.
- Explain why liquid scintillation is very efficient for detecting beta particles.
- Identify different sources of background radiation in liquid scintillation.
- Describe how to prepare a quench curve and how to determine the efficiency of a sample based on the quench curve.
- Review a liquid scintillation spectrum and identify different components of that spectrum.